

Synthesis of Benzil and its Various Derivatives

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Abstract - Benzil (systematically known as 1,2-diphenylethane-1,2-dione) is the organic compound with the formula $(C_6H_5CO)_2$, generally abbreviated $(PhCO)_2$. This yellow solid is one of the most common diketones. Its main use is as a photoinitiator in polymer chemistry.

Most benzil is used in the free-radical curing of polymer networks. Ultraviolet radiation decomposes benzil, generating free-radical species within the material, promoting the formation of cross-links. Benzil is a potent inhibitor of human carboxylesterases, enzymes involved in the hydrolysis of carboxylesters and many clinically used drugs.

Key Words: benzil, benzilic acid, Mesohydrobenzoin, dibenzyl, Diketone.

1. INTRODUCTION

Diketone is a molecule which contains two ketone carbonyl groups. Benzil is simplest aromatic diketone. It is an alpha – diketone which has two ketone groups side by side. Usually alpha – diketone imparts a caramel like a or butter flavour. Dieketone compounds take a role in creating various fragrances. Benzil is used as a precursor to the battle field chemical weupon the anticholinergic deliriant BZ which is chemical 3 quinuclidinol benzillate. Its active in mid-microgram levels and causes 3 days or more of intensely realistic and unpleasant delirial hallucinations.

1. This diketone is used as an intermediate in organic synthesis.
2. Benzil is also employed as a photoinitiator for free-radical curing of polymer networks. Ultraviolet radiation decomposes benzil, creating free-radical species which propagate throughout polymer material, creating cross-links between individual polymer chains.
3. Recently benzil has been identified as a selective inhibitor of carboxylesterases enzymes, proteins involved in the metabolism of esterified drugs and xenobiotics.

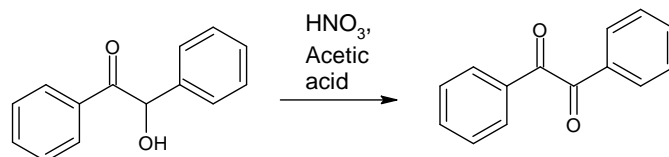
1.1 Preparation of Benzil

Procedure:-

Place 2.0 g (0.094 mol) of the crude benzoin (Section IV, 154) and 10ml of concentrated nitric acid in a 250-ml round-bottomed flask. Heat on a boiling water bath (in the fume cupboard) with occasional shaking until the evolution

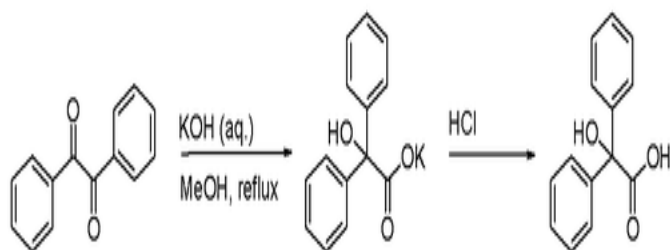
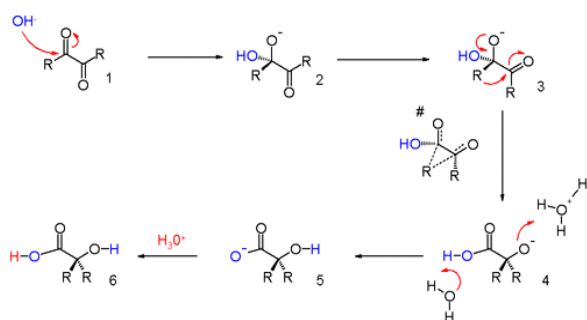
of oxides of nitrogen has ceased (about 1.5 hours). Pour the reaction mixture into 300-400 ml of cold water contained in a beaker, stir well until the oil crystallizes completely as a yellow solid. Filter the crude benzil at the pump, and wash it thoroughly with water to remove the nitric acid. Recrystallise from ethanol or rectified spirit (about 2.5 ml per gram). The Yield of pure benzil, m.p. 94-96o C, is 1.9 g.

Reaction:-



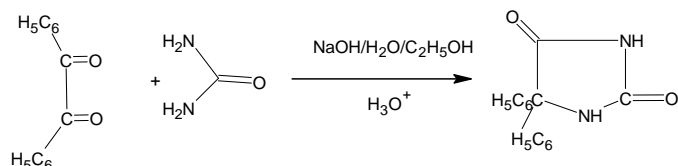
1.2 BENZILIC ACID

Procedure:- In a 500-ml round-bottomed flask, place a solution of 3.5 g of potassium hydroxide in 7.0 ml of water, then add 9.0 ml of rectified spirit and 3.5 g (0.167 mol) of recrystallized Benzil (preceding Section). A deep bluish-black solution is produced. Fit a reflux condenser to the flask and heat the mixture on a boiling water bath for 10-15 minutes. Pour the contents of the flask and heat the mixture on a boiling water bath for 10-15 minutes. Pour the contents of the flask into a porcelain dish and allow to cool, preferably overnight. The potassium salt of benzilic acid crystallizes out. Filter off the crystals at the pump and wash with a little ice-cold alcohol. Dissolve the potassium salt in about 35.0 ml of water, and add 1 ml of concentrated hydrochloric acid from a burette slowly and with stirring. The precipitate thus produced is coloured red-brown and is somewhat sticky. Filter this off; the filtrate should be nearly colourless. Continue the addition of hydrochloric acid with stirring until the solution is acid to Congo red paper. Filter off the benzilic acid with suction, wash it thoroughly with cold water until free from chlorides and allow to dry. The yield of crude benzilic acid, which is usually light pink or yellow in colour, is 3.0 g (79%). Purify the product either by recrystallisation from hot benzene (about 6 ml per gram) or from hot water with the use of a little decolourising may be recrystallised from hot water with the addition of a little decolourising carbon, and a further 1.2 g obtained. Pure benzilic acid has m.p. 150o C.

Reaction :-

Mechanism :-

1.3 Synthesis of 5, 5-diphenyl hydantoin from benzil

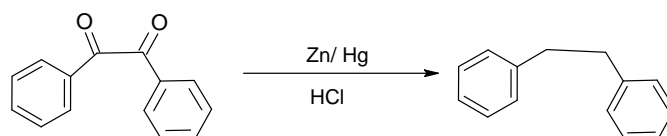
Procedure: - In a 100 ml round bottom flask fitted with a reflux condenser place 2.65 gm of benzil, 1.5 gm of urea, 8ml of 30% aqueous sodium hydroxide solution and 40ml of ethanol. Reflux the mixture on sand bath for 2 hours. Cool the mixture at laboratory temperature and then pour with stirring in a 200ml beaker containing 50 ml of water. Filter and acidify the filtrate with concentrated hydrochloric acid and then cool the acidic solution in an ice bath. Filter the precipitated 5, 5 diphenyl hydantoin on Buchner funnel and recrystallise from alcohol, m.p 297-2980 C (Yield 1.0-1.5gm).

Note : It is an important anticonvulsant used to treat epilepsy. Sodium salt of 5, 5 diphenyl hydantoin is known as Dilantin sodium.

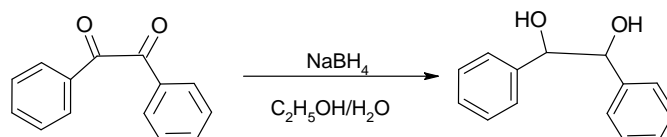
Reaction:-

1.4 Reduction of Benzil to Dibenzyl

Sr. No	Time In (hrs)	Yield (%)	M.P.(°C)
1	1.5	84%	94°C [96°C]
2	15 Min	83.55%	148°C [150°C]
3	2	91.92%	297°C [298°C]
4	5	92%	51°C [52°C]
5	30 Min	94%	136°C [137°C]

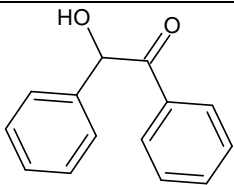
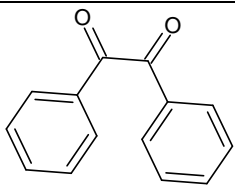
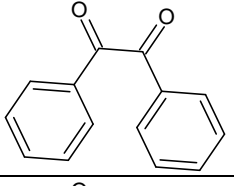
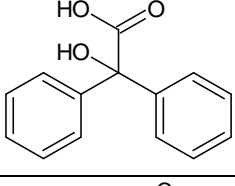
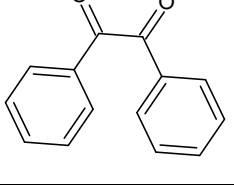
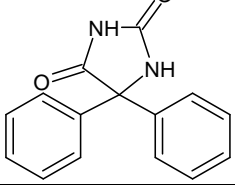
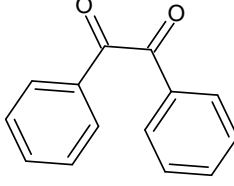
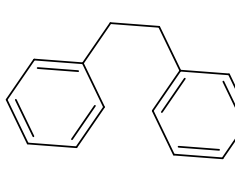
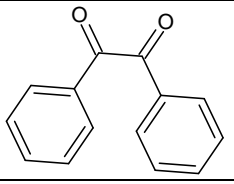
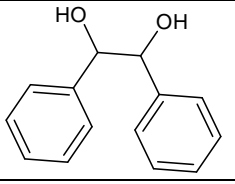
Procedure:-In a 250ml round bottom flask fitted with a reflux condenser place 1.5 gm of benzil, 6.0gm of amalgamated zinc, 22.5ml of 50% hydrochloric acid. Boil the mixture under reflux for 5 hours. Add 0.5ml of concentrated hydrochloric acid to the reaction mixture after every hour during the refluxing period in order to maintain the concentration of the acid. Cool the mixture and allow it to settle at room temperature. Decant off the unreacted zinc and transfer the filtrate to 250ml separating funnel. Add 2.5ml ether to the funnel and shake vigorously. Remove the ethereal layer and repeat the process twice, each time using 2.5ml of ether. Combine the three ethereal layers and dry over anhydrous sodium sulphate. Concentrate the dried ether extract and cool it in an ice bath, bibenzyl slowly crystallizes out, m.p 52° C (Yield 8-9 gm).

Reaction:-

1.5 Reduction of Benzil to Mesohydrobenzoin

Procedure:-In a 100ml conical flask dissolve 2.5gm of benzil in 25ml of ethanol and cool. Then add 1 gm of sodium borohydride, the mixture becomes warm and the yellow colour disappears within 2-3 minutes. After 10 Minutes add 0.5ml of water to the reaction mixture and warm the conical flask on water bath so that the mixture begins to boil. Cool the flask in ice bath and collect mesohydrobenzoin on Buchner funnel. Recrystallise from alcohol, m.p136-1370 C(Yield 1.5.0-1.7gm).



2. Results

Sr. No	Reactant	Product
1		
2		
3		
4		
5		

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3. CONCLUSIONS

Diketones are most widely used as a photoinitiator in synthesis of polymers which are advanced materials.

Above reactions indicates synthesis of benzil and its derivatives are simple. Product formation rate is high. Time duration of reactions is also less.

4. REFERENCES

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